

Production and Characterization of Nylon-6 Filaments Containing Carbon Black*

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Nylon-6 filament yarns containing up to 1.5% carbon black have been prepared using two different methods, viz. (1) incorporating carbon black in disperse form during polymerization and melt spinning, and (2) blending the chips containing 1.5% carbon black, prepared as in (1), with chips without any carbon black (blank) and melt spinning. The filaments thus produced were examined for their structure and properties. It has been observed that the samples prepared by method (1) are more homogeneous and have more uniform properties.

Synthetic fibres can be coloured to black and grey shades by incorporating carbon black into the polymer before spinning. The incorporation of carbon black into the polymer can be achieved by three methods^{1,2}: (i) Adding a slurry containing carbon black into the monomer feed, (ii) Preparing a master batch of chips containing a high amount of carbon black by method (i) and then mixing mechanically with the blank chips during spinning, and (iii) Injecting a special formulation containing carbon black into the melt stream just prior to spinning.

In the first method, carbon black dispersed in water with the dispersing agent is added to the caprolactam melt. For higher concentrations of carbon black, water-caprolactam mixture is taken instead of water. The polymer thus produced is converted into chips.

In the second method, a master batch of chips containing a high amount of carbon black is prepared as above and then mixed with blank chips in different proportions before spinning to get the desired shade.

The third method involves the use of special formulations with a high carbon black content which are injected in the melt spinning unit, so that the blank chips melt together with the concentrated injected material to produce filaments containing carbon black.

In the present investigation, nylon-6 filaments containing various amounts of carbon black have been produced by the first two methods and their structure and properties have been studied systematically.

Experimental Procedure

Polymerization—The polymerization was carried out in a bench scale polymerization unit (Fig. 1).

Carbon black (average particle size, 25 μm) was ball-milled in water containing sodium naphthalene sulphonate (10% by wt of carbon black) as the dispersing agent. The main

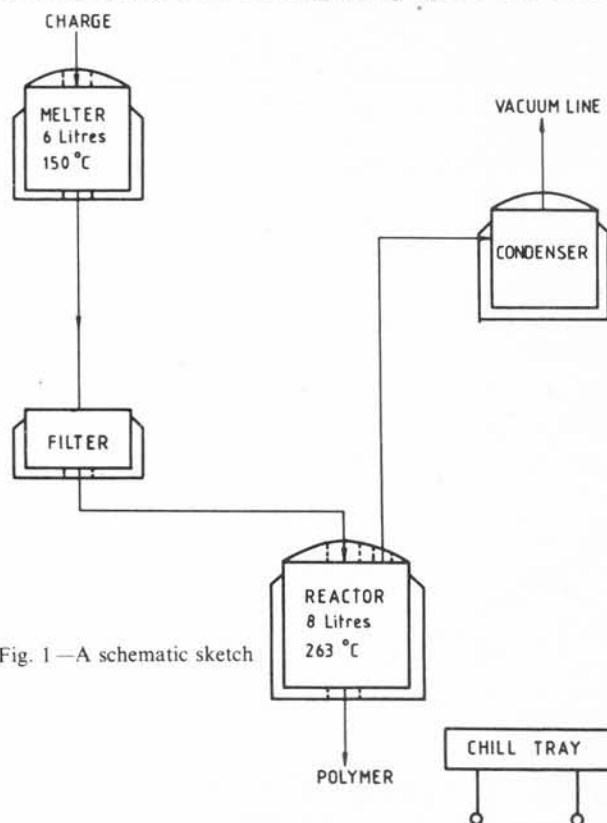


Fig. 1—A schematic sketch

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purpose of ball milling was to break down the agglomerates of carbon black particles. The samples of slurry were collected at various time intervals during ball milling and their optical density was determined. The dependence of the optical density of the slurry at a fixed wavelength on the duration of ball milling is shown in Fig. 2. On the basis of this plot, the duration of ball milling was determined.

Molten caprolactam (5 kg) was charged in the polymerization reactor, followed by carbon black slurry containing water (220 ml) prepared as above. Polymerization was carried out in the conventional manner³ with pressure (up to 7.5 kg/4 hr) and vacuum (300 torr/3.25 hr), the transition from pressure state to vacuum state being achieved in 2 hr. Thus, the total duration of polymerization was 9.25 hr. The polymer melt was extruded into strands, cut into chips, extracted with boiling water to remove the monomer and oligomers, and dried. The dried chips had the following specifications:

Average chips size	= diam., 1.5 mm; length, 2 mm
Relative viscosity (25°C, 96% H ₂ SO ₄ , 1% wt/wt conc.)	= 2.2 ± 0.05
Moisture content	= <0.04%
Melting point	= 215°C

Melt spinning—The normal procedure⁴ for melt spinning of nylon-6 was used. The Fuji melt spinning tester type C, which is an extruder spinning unit, equipped with a screw, a metering pump, a cooling chimney and a take-up device, was used to melt-spin monofilaments from the dried polymer chips.

A double tube type filter having a 18 mm diam. tube over a 14 mm diam. tube and with a pore size of 40 μ m was fitted in the spin pack along with a monohole spinneret with an orifice of 0.5 mm diam. and 1.0 mm length. The temperature of the barrel was set at 270°C

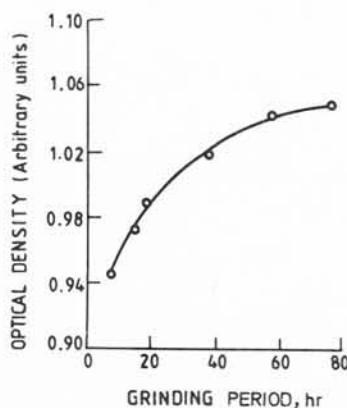


Fig. 2—Optical density of carbon black slurry versus ball milling period

and that of spin pack at 263°C. A constant flow of air at 25°C was maintained through the chimney to quench the filaments. The yarn was passed through a trough containing the spin finish and was collected on a take-up unit at a speed of 278 m/min.

Draw twisting—The filament yarns were conditioned (25°C, 65% RH, 8 hr) and draw twisted on a commercial draw twister at a draw ratio of 3.26. Two sets of filament yarns were prepared:

Set A—Filaments from chips containing carbon black (polymerization technique).

Set B—Filaments from the mixture of blank and chips containing 1.5% carbon black (master batch technique).

In each set, the following seven samples were prepared:

Sample No.	Carbon black content, % (by wt)
1	0
2	0.03
3	0.075
4	0.15
5	0.30
6	0.75
7	1.5

Knitting of tubes—Tubes were knitted from the filaments on a conventional socks knitting machine using two filaments together.

Measurement of colour—The colour of the knitted samples with reference to the sample containing no carbon black was measured as reflectance in the three CIELAB coordinates L, A and B using Photo Match PM 300 of Photo Maker Corporation, USA.

Measurement of density—The density (ρ) of the fibres was determined by the flotation method using Davenport density gradient column. The column was prepared using the mixture of carbon tetrachloride ($\rho = 1.590$ g/ml) and xylene ($\rho = 0.875$ g/ml) and measurements were made at 25°C.

X-ray diffraction studies—The crystallinity was determined using an X-ray diffractometer as per the method suggested by Stepanaik *et al.*⁵. For this, measurements were made on fine random sample obtained by cutting the filaments.

Differential scanning calorimetry—The thermal characteristics of the fibre samples were evaluated using Du Pont's differential scanning calorimeter under the following conditions: Temperature range, 100–250°C; heating rate, 10°C/min; sample wt, 7–8 mg; atmosphere, air; and reference, empty pan.

The instrument gave plots of enthalpy change (ΔH) as a function of temperature. From the shape of the melting curve, information about the melting range

and, more specifically, the melting point, could be obtained. The half-width of these curves, normalized to equal area, was taken as a measure of the crystal size.

Limiting oxygen index—Knitted tubes were fixed on a frame and kept in the chamber of a Stanton flammability tester. The oxygen-nitrogen ratio was so adjusted that the sample, when exposed to flame, just sustains burning. The limiting oxygen index was read from the digital display.

Mechanical characteristics—The load-elongation curves of monofilaments (gauge length, 5 cm) were obtained on the Instron tensile tester at an extension rate of 100% per min. Twenty-five tests were made on each sample. The load-elongation curves were converted to stress-strain curves. For calculating stress, load was divided by the initial denier of the filament. From the stress-strain data, the following parameters were computed:

(1) Young's modulus was obtained from the initial slope of the stress-strain curve.

(2) Elongation-at-break (%) was calculated using the following expression:

$$\text{Elongation, \%} = \frac{\text{Change in length}}{\text{Original length}} \times 100$$

(3) Tenacity was obtained by dividing the breaking load with the initial denier of the filament.

The sonic modulus was measured using pulse propagation meter PPM-5R (H.M. Morgan, USA) equipped with a fibre scanner. The filament yarn was held fixed at one end and loaded at the other with 9.5 g, so that it was under tension. The sonic velocity was calculated from the plot obtained on the strip chart recorder and the sonic modulus (E) was calculated using the relation $E = \rho C^2$, where ρ is the density of the filament and C , the sonic velocity.

Photodegradation—Photodegradation of the samples was carried out by exposing the fibres mounted on a board in Atlas Fade-O-meter having MBTF Philips 500 watt mercury lamp. The samples were exposed for 24 hr and the mechanical characteristics of the exposed samples were evaluated as described earlier.

Weathering—The samples were mounted on aluminium sheets and exposed to natural light. The location was so selected that the shadows of the surrounding objects did not fall on the exposed specimen. The samples faced south and were at an angle of 45° to the horizon. The samples were kept exposed all the 24 hr of the day for 2-8 weeks. The mechanical characteristics of the exposed samples were evaluated as described earlier. The reduced viscosity was measured at 25°C by preparing 1% solution in 96% H_2SO_4 .

Moisture regain—The moisture regain of the fibres was determined by conditioning the fibres for 8 hr at $65 \pm 2\%$ RH and $25 \pm 2^\circ\text{C}$. The fibres were then weighed and kept in a vacuum desiccator over phosphorous pentoxide for 3 days and weighed again. Repeated weighings were done till a constant weight of the fibre was obtained. From the difference in weight, moisture regain (%) on the dry weight basis of the fibre was calculated.

Results and Discussion

The results are presented in Tables 1-5 and Figs 3-10.

The CIELAB darkness values for set A and set B are similar (Table 1). The darkness value is decided, apart from the concentration of the pigment, by its average particle size and size distribution. Since the two sets exhibit a similar darkness level, it can be concluded that the average particle size and the size distribution at any carbon black concentration are not influenced by the method of production of the carbon black-filled fibres.

The density values for the different filament samples (Table 2) indicate that there is a marginal increase in density for the filled samples. The density of carbon black is 1.8-2.1 g/cm³, while that of nylon-6 is 1.138 g/cm³.

The $I-2\theta$ plots for two representative filament samples obtained from the diffractometer are shown in Fig. 3. From these, the X-ray crystallinity index has been computed and it has been observed that the X-ray crystallinity indices of these samples are almost similar. These data indicate that the presence of carbon

Table 1—Darkness Values (CIELAB Scale)

Sample No.	Set A	Set B
1	0	0
2	5.6	5.0
3	11.0	10.9
4	15.0	15.2
5	18.8	18.8
6	20.3	19.4
7	20.4	20.4

Table 2—Densities of Filament Samples

Sample No.	Density, g/cm ³	
	Set A	Set B
1	1.138	1.138
2	1.138	1.138
3	1.139	1.141
4	1.139	1.143
5	1.138	1.143
6	1.141	1.143
7	1.140	1.140

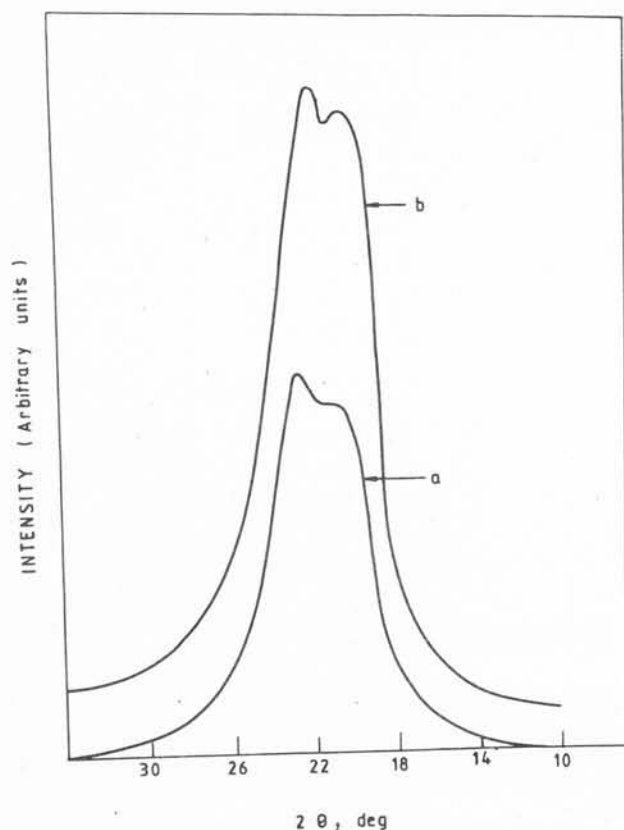


Fig. 3— $I-2\theta$ diffractograms for (a) blank sample, and (b) sample containing 1.5% carbon black (sample A-7)

black and the method of preparation do not influence the crystallinity index to any significant extent.

Typical differential scanning calorimeter (DSC) thermograms for the two sets of fibre samples are shown in Figs 4 and 5. The heat changes associated with the melting process for set A samples (Fig. 4) are spread over more than 20°C having the melting peak in the range $220-223^{\circ}\text{C}$. The set B samples exhibit almost similar behaviour (Fig. 5). However, in the thermograms of set B samples 5 and 6, the composite nature of the peak is clearly apparent, which is not so in the case of set A. This may be indicative of the fact that in set B there are two phases which melt at different temperatures. While it is difficult to define the two phases, it is possible that non-uniform mixing could give rise to these two phases, one phase being close to the matrix material and the other to carbon black-filled material. It is known that the filler particles can act as nuclei and affect the crystallization behaviour. If the carbon particles are non-uniformly distributed, this heterogeneous nucleation can result in the growth of small crystallites and these will melt at a lower temperature. Thus, set B samples, which were produced by the master batch technique, appear to be more heterogeneous than set A samples.

The difference in crystallinity of the various samples was found to be insignificant. Thus, it is likely that the differences in DSC melting peaks arise from the difference in the crystal sizes and distribution between

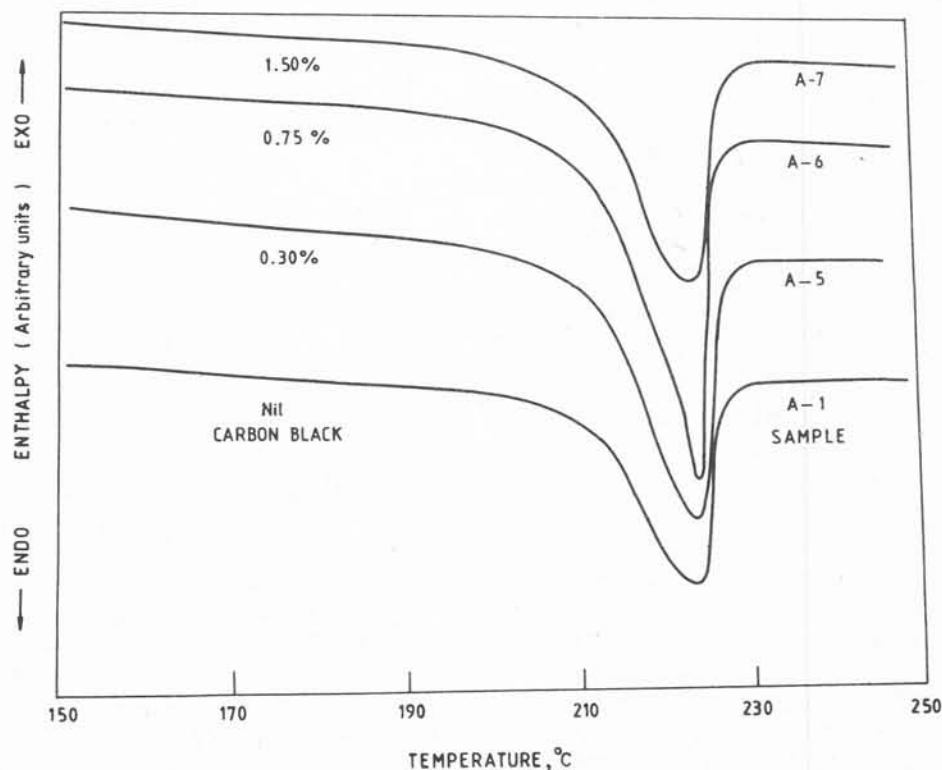


Fig. 4—Differential scanning thermograms for set A samples

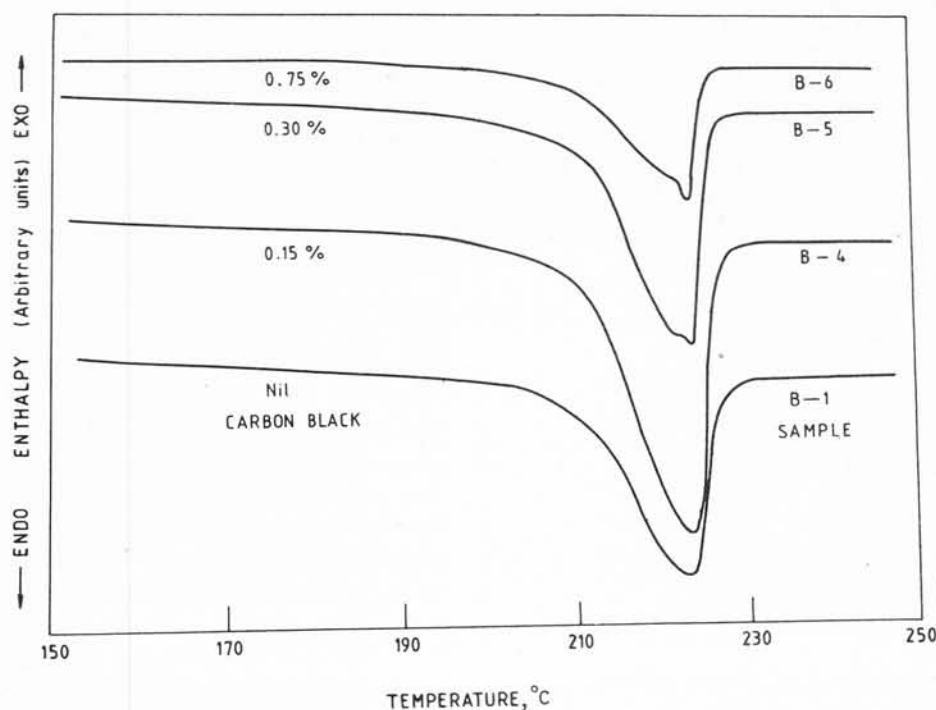


Fig. 5—Differential scanning thermograms for set B samples

Table 3—Half-Width of Melting Peak (°C)

Sample No.	Set A	Set B
1	10	10
4	—	9.35
5	9.13	9.35
6	7.17	8.26
7	9.13	9.13

the various samples. Since the half-width of the normalized melting peak would be related to crystal size, the data have been analyzed for half-width and a decrease in half-width for samples containing carbon black has been observed (Table 3). This is indicative of small crystal size, which, in turn, arises from the larger nucleation sites available in carbon black-filled polymer.

The limiting oxygen index (LOI) appears to increase slightly with carbon black content (Table 4). It is known^{6,7} that carbon black acts as a free radical absorber. This protective mechanism may be operative during ignition of the filaments in LOI test, partly accounting for the higher values of LOI for carbon black-filled fibres. The LOI is slightly higher for set B samples compared to set A samples. This observation may be explained on the basis of heterogeneity; in a heterogeneous structure, the carbon black-filled phase may be more effective in reducing the flame propagation, because regions having higher carbon black content will be present in these samples.

Table 4—Limiting Oxygen Index of Nylon-6 Filaments

Sample No.	Limiting oxygen index	
	Set A	Set B
1	27.0	27.0
2	27.8	27.8
3	27.6	28.0
4	27.3	28.1
5	27.3	28.2
6	27.8	28.2
7	28.0	28.0

The samples with carbon black show a lower modulus, lower tenacity and, in general, higher elongation-to-break than the blank sample (Figs 6 and 7). This indicates that the small quantity of carbon black, present in the sample, does not act as a reinforcing agent, but, on the other hand, appears to weaken the structure. With increase in carbon black content, the tenacity and modulus decrease, while elongation-to-break does not show a clear trend. The presence of carbon black results in relatively higher percentage reduction of the initial modulus measured on Instron compared to the sonic modulus. This is indicative of the role of the viscoelastic effects arising from the amorphous regions where the carbon black will be expected to reside. The carbon black particles, due to lack of interaction with the matrix, act as inert fillers and, therefore, when present in small amounts, do not reinforce the matrix material.

The CV % calculated for the mechanical characteristics of 25 samples indicates that set B samples show relatively higher non-uniformity than set A samples (Table 5).

The results of the weathering and exposure experiments carried out on samples of set B are shown in Figs 8 and 9. Corresponding studies on set A samples were not made. The viscosities of the original (unexposed) samples exhibit a slight decrease with increase in carbon black content (Fig. 8). The viscosity of each sample is reduced with increasing period of weathering. The maximum reduction in viscosity for any weathering period is around the carbon black content of 0.15%. The tenacity data (Fig. 9) show a similar trend for the corresponding samples. Since carbon black is known to be an ultraviolet stabilizer^{6,7}, it is expected that the mechanical characteristics of the fibre and its viscosity will not deteriorate appreciably in the presence of carbon black. In the accelerated weathering test done by exposing the samples in a Fade-O-meter, this expected trend is obtained. But in long term weathering, the presence of carbon black

does not appear to protect the fibres as efficiently. In long term weathering, other factors, such as non-uniformity of the fibre structure, moisture regain, variations in day and night temperatures and humidity, are also important. The moisture regain of the samples (Fig. 10) indicates that the samples containing carbon black absorb less moisture, the minimum absorption being at 0.15% carbon black content. The inability of carbon black to offer protection in this set of samples could be due to the non-uniform distribution of carbon black, resulting in structural non-homogeneity.

Table 5—CV (%) in Mechanical Characteristics

Sample No.	Tenacity		Elongation		Modulus (Instron)	
	Set A	Set B	Set A	Set B	Set A	Set B
1	4.8	4.8	5.8	5.8	4.9	4.9
2	5.7	9.6	7.7	10.2	5.4	9.0
3	5.0	7.9	5.7	7.8	5.3	7.4
4	6.2	6.2	5.2	7.9	5.0	6.1
5	7.4	6.6	6.2	6.4	6.8	6.3
6	7.4	7.5	7.4	7.4	6.9	7.00
7	5.7	5.7	7.4	7.4	6.0	6.0

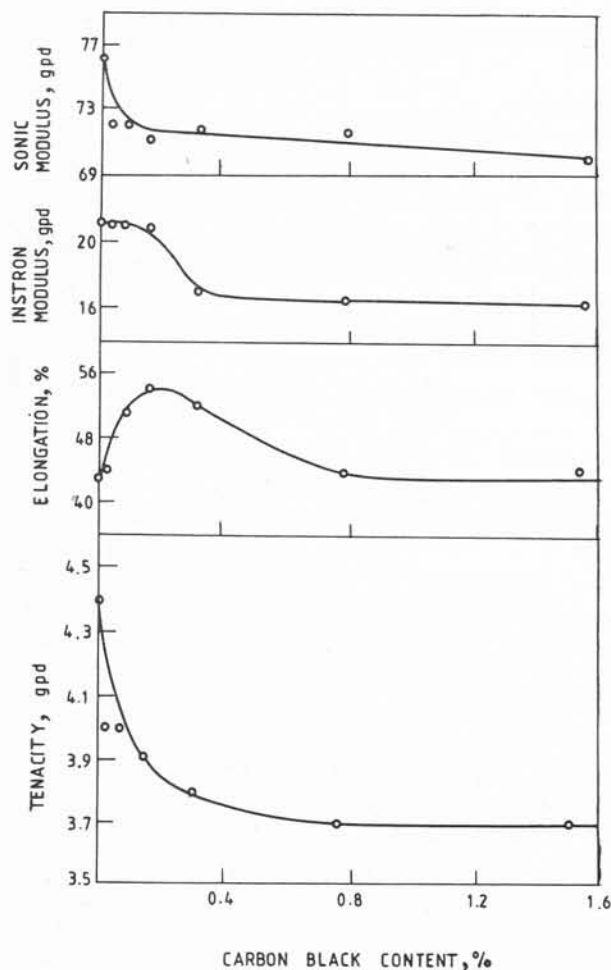


Fig. 6—Mechanical characteristics of set A samples

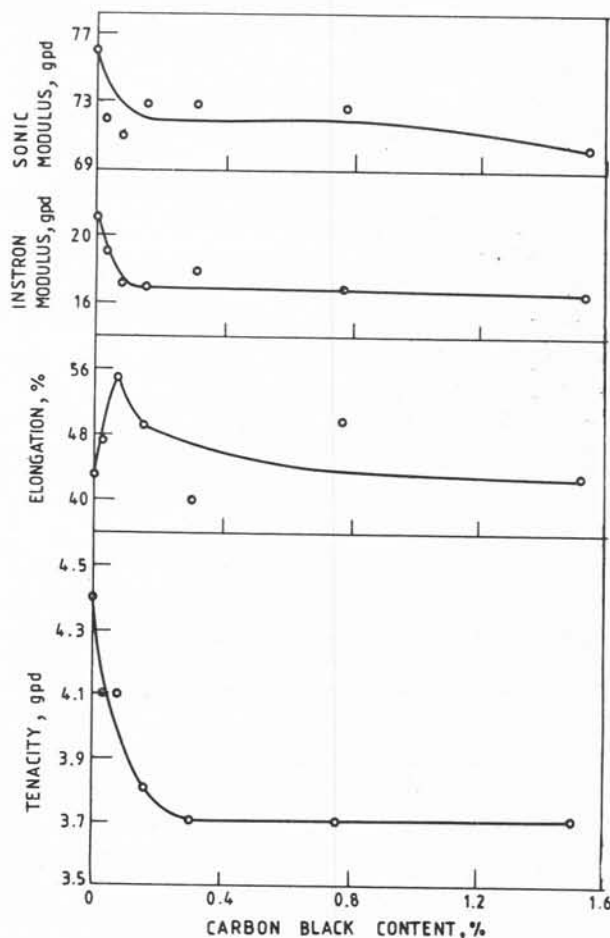


Fig. 7—Mechanical characteristics of set B samples

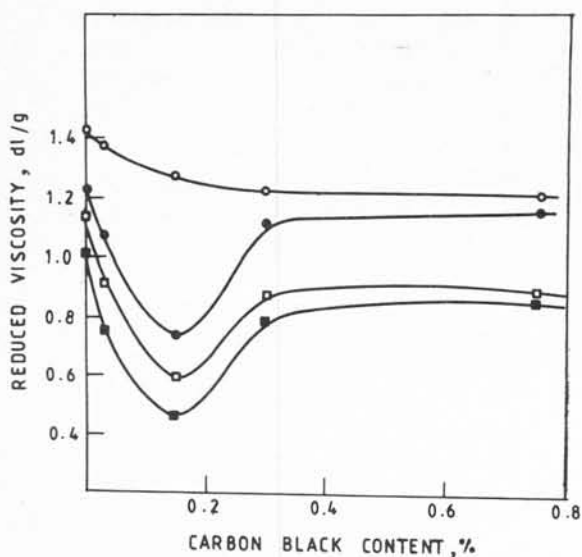


Fig. 8—Reduced viscosities of samples versus carbon black content [(○) original, (●) weathered for 2 weeks, (□) weathered for 4 weeks, and (■) weathered for 8 weeks]

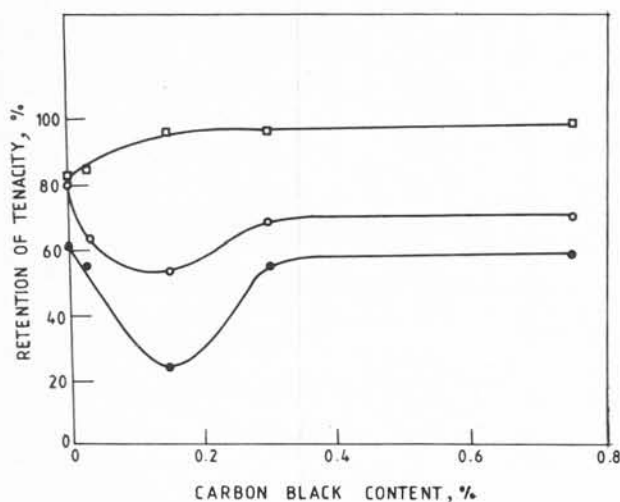


Fig. 9—Change in tenacity in the exposed samples versus carbon black content [(□) exposed in Fade-O-meter for 24 hr, (○) weathered for 4 weeks and (●) weathered for 8 weeks]

It has already been stated that the CV % values for the mechanical characteristics (Table 5) of set B samples are higher than for set A samples. Within set B itself, the various samples have been prepared with the following proportions of blank: master batch—98:2, 95:5, 90:10, 80:20 and 50:50. For samples with small or comparable proportions of master batch, the CV % is relatively low. The weathering data (Figs 8 and 9)

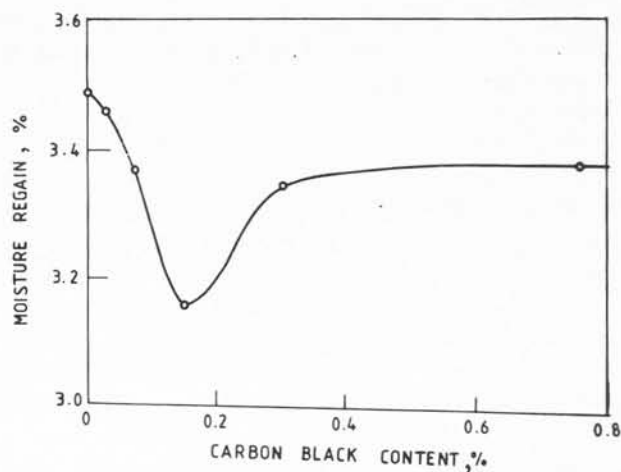


Fig. 10—Moisture regain of set B samples versus carbon black content

indicate that for these samples, degradation is also relatively less. These observations imply that homogeneity is relatively better in set B samples, indicating that mixing has been more efficient in the case of these samples. This aspect has not been studied in detail and, therefore, no further comments are made.

Conclusion

It is possible to produce a series of grey-black nylon-6 filaments in a convenient manner using the master batch technique. This technique does not give a filament as uniform as that produced by incorporating carbon black into the polymer during the polymerization. The samples produced by master batch technique appear to exhibit two-phase heterogeneous structure, which has a considerable influence on their structure and properties.

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